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Thermal and electrical conductivities of alloys at low temperatures.

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An apparatus for the simultaneous measurement of the electrical and thermal conductivities of metals and alloys at low temperatures has been described. A combined differential and absolute manometer has been designed for the measurement of the temperature gradient along a rod of the substance and also the absolute temperature at a point of the rod. The temperature of the bath is controlled by pumping liquid hydrogen, liquid nitrogen or liquid oxygen under controlled pressure through a Cartesian manostat.

Experiments have been made with two samples of copper alloys containing 1.96% Zn and 4.76% Zn respectively and the thermal conductivity data have been utilised to calculate separately the lattice and electronic parts with the help of electrical resistivity data, simultaneously taken on the same sample. The lattice thermal conductivity values thus obtained have been interpreted in terms of modern theories.

1. Introduction

The study of electrical and thermal conductivities of alloys at low temperatures has been the subject of many investigations (Hulm 1951 ; Berman 1951; Estermann & Zimmerman 1952; Kemp *et al* 1957 ; Lomer & Rosenberg 1959 ; Backlund 1961 ; Lindenfeld *et al* 1962 ; Garber *et al* 1963 and Charsley 1968). In the earlier investigations of the thermal conductivities at low temperatures the attention was mainly confined to metals (Rosenberg 1954, 1956, 1957 ; White 1953 ; White & Woods 1959) where the electronic part of the thermal conductivity was so predominant that the thermal conductivity due to lattice vibration could be neglected.

Recently, however, theoretical studies by Klemens and others (Klemens 1958) have shown that the thermal conductivity due to lattice vibrations is quite interesting because it gives different T—variations in different ranges of temperature on account of the different types of interaction of the phonons with the electrons, grain boundary, point defect, dislocation, etc. In fact, the lattice thermal conductivity K_g, can be represented (Mendelssohn & Rosenberg, 1961) by the relation

$$\frac{1}{K_g} = W_g = W_{g'} + W_B + W_P + W_U + W_{dis}$$
$$= ET^{-2} + BT^{-2} + PT + gT^n e^{-\theta/\alpha T} + DT^{-2} \quad \ldots(1)$$

where the subscripts refer to the scattering of phonons by electrons, specimen and grain boundaries, point defects and isotopes, Umklapp process, and dislocations respectively. The equation shows that the

lattice thermal conductivity due to different interaction processes have, in general, widely different T—variations and therefore, it becomes possible to separate the ranges in which a particular interaction becomes predominant. Therefore, the study of the lattice thermal conductivity becomes a powerful method for studying the various types of interactions of phonons from which it is possible to have a knowledge of the imperfections in that particular substance.

However, since the experimental measurement of thermal conductivity has yet attained only limited accuracy, the separation of the contribution due to lattice thermal conductivity is almost impossible in pure metals because of the large values of electronic thermal conductivities. Hence it is desirable to reduce the electronic part to such an extent that it becomes comparable to the lattice thermal conductivity. This can be done by various methods (Klemens 1958) of which the alloying of the metal by some other impurities has been the most successful. The electronic thermal conductivity of the alloy is found out from the simultaneous measurement of the electrical resistivity of the sample and making use of the Wiedemann-Franz law to calculate the electronic thermal resistivity due to impurities.

In this work we have measured the thermal conductivity of two alloys of copper containing 1.96% Zn and 4.76% Zn respectively. Copper-zinc alloys have been previously investigated by Kemp, Klemens & Tainsh (1957) and Klemens, Klemens, Tainsh and White (1957) and the data have been analysed by White (1960) to explain the observed variation of W_i with temperature in terms of W_u and W_p, but the explanation is hardly satisfactory.

2. Description of the apparatus

The design of the cryostat is essentially similar to that of White & Woods (1955). The schematic diagram of the cryostat is shown in figure 1. The outer cylindrical can of brass, having a diameter of 8.5cm., is suspended from the top plate by means of stainless steel pumping tubes. These tubes are soft soldered through bushes of brass which are hard soldered into the plates. The outer can is joined with Wood's metal at X so that it can be easily removed and replaced after mounting the specimen. The inner copper shield (chromium plated) is attached to the heat sink by screwing the shield at the joint marked Y. The electrical leads and the thermometer capillary tubes are taken out through the slot Z. The refrigerating liquid can enter the copper chamber through the inlet valve V which consists of a stainless steel needle of 10° total taper seating in a brass shoulder and is operated by turning the knurled head above the main top plate.

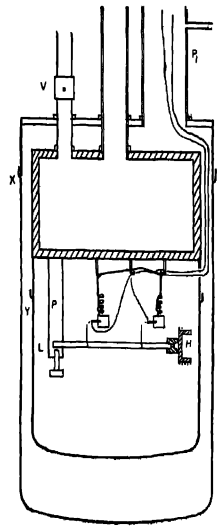

Figure 1. Schematic diagram of the cryostat for the measurement of thermal coductivity.

The specimen is mounted horizontally by screwing and soldering one end into a hole *L* drilled in the copper pillar *P*, the latter being hard soldered to the heat sink. A hearter *H* is fixed at the other end of the specimen by Wood's metal. The heater is made of silko-ribbon constantan resistance which is fixed to a copper performer by glyptal. It isproperly baked and dried to ensure good thermal contact and at the same time good electrical insulation. For potential leads, which serve also as thermometer leads, two short lengths of copper wire are tightly wrapped round the specimen at two points, and then soldered to it. This gas thermometer bulbs of copper are gold plated to prevent tarnishing and also to keep the radiation correction small and constant. They are connected by cupronickel capillary tubing to the external manometer system. To avoid electrical short-circuit through these thermometers and their supporting capillaries both the thermometers are electrically insulated from the specimen but thermally well-connected. This is done by covering the copper strip (1/16 in. x 1/64 in.) attached to the thermometer bulbs with a layer of glyptal and cigarette paper, baking the varnish, adding fresh varnish and then wrapping this layer with copper foil and finally baking it to harden

the varnish (figure 2). The copper potential leads from the specimen are then attached by Wood's metal to this foil. For simultaneous measurement of electrical conductivity current leads are also soldered at the two ends of the specimen.

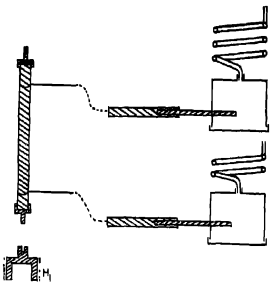

Figure 2. Method of mounting thermal conductivity specimens.

The inner and outer containers are evacuated during the thermal and electrical conductivity measurements through a common pumping line P_1 as shown in figure 1. All electrical and thermal leads are brought through the pumping line P_1 and araldite is used to seal the top of the tube from where the leads are taken out. The electrical resistivity is measured with the help of an accurate potentiometer reading upto 10^{-8} volt in conjunction with a photocell galvanometer amplifier (type 5214) supplied by M/s. H. Tinsley & Co. Ltd., London.

(*a*) *Measurement of temperature and the thermal gradient.*

Helium gas therometers have been used to measure the absolute temperatures as well as temperature gradient along the specimen. For the measurement of temperature gradient a butyl phthalate manometer similar to the one described by Hulm (1950) has been employed (figure 3). In the present arrangement however, the sensitivity of the differential thermometer has been increased by using mercury for total pressure measurement and oil for differential measurement. This is a modification of the arrangement described by Mendelssohn and Pontius (1937) in which mercury manometer and differential manometer were separated. In our set up, both are connected whereby compactness has been achieved although at the cost of a slight error in the measurement of the absolute temperature.

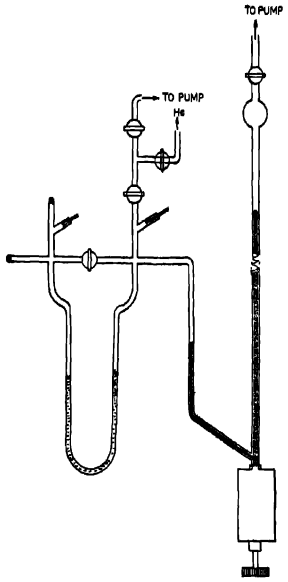

Figure 3. Combined differential and absolute manometer for temperature measurements.

(b) Temperature control.

The temperature control of the sink is usually done by (a) vapour pressure control and (b) electrical heating. In the present work, we have only employed vapour pressure control.

The vapour pressure has been controlled by means of a Cartesian manostat discussed in detail by Gilmont (1946, 1951). The design shown in the figure 4 is convenient to construct and handle. It consists of a glass dewar *D* of about 1 in. diameter. This is $\frac{1}{4}$ in. smaller in outside diameter than the internal diameter of the main tube. The diver has several glass pips suitably attached for centering. A valve is formed by a glass orifice *P* (1 mm. dia) seating and unseating against a rubber pad attached to the diver. During operation, the desired pressure above the liquid is attained by pumping through a bypass value and keeping the glass stopcock *G* open. Then the bypass valve and *G* are both closed and the pressure remains steady.

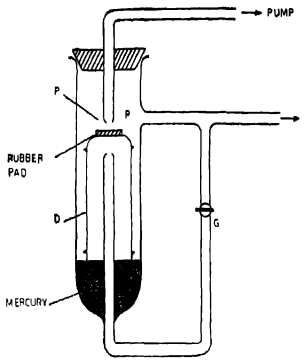

Figure 4. Cartesian manostat of glass for temperature control.

(c) Preparation of the alloys.

The alloys were prepared from spectrographically pure rods of copper and zinc, supplied by Messrs. Johnson, Matthey & Co., Ltd., London. The metals in appropriate proportions were sealed in an evacuated quartz tube and placed in a furnace and the temperature was raised to 1100°C. The mixture was melted and thoroughly shaken. The temperature of the furnace was then brought down to 900°C and kept at that temperature for five days to facilitate complete mixing of the two components. The alloy was then rolled in rod form and annealed in evacuated sealed glass tubes at about 500°C for six hours. The samples were then ready for mounting in position.

3. Results and discussion.

Measurements of the thermal conductivity of the specimens were taken in the temperature regions of 16°K to 20°K and 60K° to 90°K. These results are plotted in figure 5 and the best curves have been drawn through these observed points. The gaps between the two temperature ranges were bridged by interpolation. The electronic thermal conductivity K_e is given by

$$\frac{1}{K_e}=W_e=W_i+W_0, \qquad \ldots(2)$$

where W_i and W_0 are ideal and residual thermal resistivities respectively. W_0 is calculated with the help of Wiedemann-Franz law

$$W_0=\rho_0/L_0T, \qquad \ldots(3$$

where ρ_0 is the residual electrical resitivity, and L_0, the Lorentz number ρ_0 is determined from the measurement of electrical resistivity of the alloys at several temperatures down to 16°K and subtracting the electrical resstivity of pure metal at the corresponding temperatures. The values of ρ_0 thus obtained were found to be constant within the limits of experimental error. The value of W_i was assumed to be unaltered by alloying and was taken from the measurements on pure metals by Po-well *et al* (1961). In tables 1 and 2, Ke and Kg values are given for different temperatures for the two alloys.

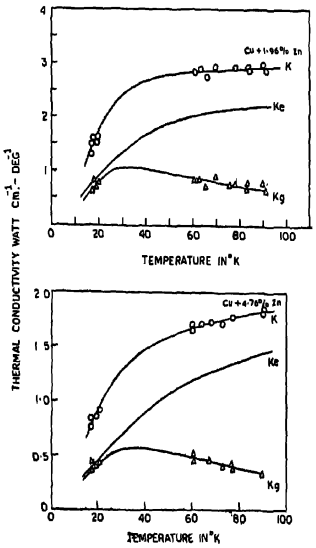

Figure 5. Thermal conductivities of Cu+1.96% Zn and Cu+4.76%Zn

The total thermal conductivity values are also listed in the tables from the smoothed experimental curves of figure 5. From these tables it can be seen that W_g/T in the temperature range of 60°K to 90°K is almost constant for particular alloy. In this region $W_{g\,s}$, W_b and W_{di} become negligible, hence from eq. (1), $W_g = W_p + W_u$. But this expression does not take into account the effect of the three phonon anharmonic interaction conserving quasi-momentum (N-process) as pointed out by Ziman (1956). The role of N-process is to maintain the equilibrium of the phonon spectrum by feeding energy from the low frequency

TABLE 1. Cu + 1.96% Zn, $\rho_0 = 5.49 \times 10^{-7}$ OHM. CM.

Temp. in °K T	Total conductivity K	Ideal resistivity W_i	Residual resistivity W_0	Electronic conductivity K_e	Lattice conductivity K_g	Lattice resistivity/Temp. W_g/T
20	1.67	.0114	1.120	.889	.786	
30	2.25	.0250	.747	1.295	.955	
40	2.55	.0503	.560	1.639	.911	
50	2.70	.0847	.448	1.576	.824	
60	2.80	.125	.373	2.008	.792	.0210
70	2.83	.164	.320	2.006	.764	.0187
80	2.87	.189	.280	2.137	.733	.0171
90	2.89	.213	.249	2.165	.725	.0171

K is in watt cm^{-1} deg^{-1}, W is in watt^{-1} cm. deg and W_g/T in watt^{-1} cm.
Mean W_g/T = .0176 watt^{-1} cm.

TABLE 2 : Cu + 4.76% Zn ; $\rho_0 = 1.043 \times 10^{-6}$ OHM. CM.

Temp. in °K T	Total conductivity K	Ideal resistivity W_i	Residual resistivity W_0	Electronic conductivity K_e	Lattice conductivity K_g	Lattice resistivity/Temp. W_g/T
20	.90	.0114	2.128	.467	.433	
30	1.24	.0250	1.419	.693	.547	
40	1.45	.0503	1.064	.897	.553	
50	1.57	.0847	.851	1.068	.502	
60	1.72	.125	.710	1.198	.522	.0320
70	1.76	.164	.608	1.295	.465	.0310
80	1.80	.189	.532	1.387	.413	.030
90	1.84	.213	.473	1.458	.382	.029

K is in watt. cm^{-1} deg^{-1} ; W is in watt^{-1} cm deg and W_g/T in watt^{-1} cm.
Mean $W_g/T = 0.031$ watt ^{1} cm.

modes, which are not scattered strongly by U-processes or point defects, into the higher frequency modes. Assuming as a general case, the effective relaxation time σ for N-processes as $\sigma = n\,\tau_u$ where τ_u is the relaxation time due to Umklapp processes, we obtain, following the same procedure as Klemens *et al.* (1962)

$$\frac{K_g}{K_u} = \sqrt{\frac{n}{n+1}}\ \frac{\omega_0}{\omega_d}\ \tan^{-1}\left(\sqrt{\frac{n}{n+1}}\ \frac{\omega_d}{\omega_0}\right) \qquad \ldots(4)$$

Here ω_d is the Debye frequency and ω_o is defined by

$$\frac{\omega_o}{\omega_d} = \left[\frac{2}{\pi} \frac{k\,v}{a^3 q_D \epsilon K_U} \right]^{1/2} \quad \ldots(5)$$

Here k is the Boltzman constant, q_D, the radius of the Debye sphere, u, the the velocity of sound and $\epsilon = \Sigma C_i \left(\frac{\Delta M_i}{M} \right)^2$ where C_i denotes mass defect concentration, M, the weighted mean of the atomic masses and ΔM_i, deviation of mass of each component from M.

For Cu-Zn alloy ΔM_i being very small, the expression $\frac{\omega_d}{\omega_o}$ becomes very small and eq. (4) can be approximated to

$$\frac{K_g}{K_u} = \frac{n}{n+1} \quad \ldots(6)$$

Now from our experimental data

$$\frac{W_g}{T} = .018 \pm .002 \text{ for Cu} + 1.96\% \text{ Zn}$$

$$= .030 \pm .003 \text{ for Cu} + 4.76\% \text{ Zn}.$$

Since the effect of point imperfection scattering due to mass difference is negligible in this case, W_g is mainly due to Unklapp processes and normal interactions, which are practically independent of the compositions for dilute alloys of the same parent metal. Hence we can assume for W_g/T the average value $.024 \pm .006$ with an experimental error of $\pm .005$. Now, the theoretical expression of W_u given by Leibfried and Schlomann (1954) is

$$\frac{1}{W_u} = 3.61\, a\, A\, \theta_D^3 / \gamma^2 T \text{ watt Cm}^{-1} \text{ deg}^{-1} \quad \ldots(7)$$

where a is the lattice constant, A, the atomic weight, θ_D, the Debye temperature and γ, the Gruneisen parameter. For copper White (1960) has assumed γ to be 2.6 where as Gruneisen's value is 2.0. The corresponding values of W_u/T are .0285 and .017 respectively. But it is clear from the expression (6) that White's value of W_u/T does not give any positive value n. We therefore select Gruneisen's value of γ and the corrcsponding W_u/T Hence from (6)

$$\frac{n}{n+1} = \frac{K_g}{K_u} = \frac{W_u/T}{W_g/T} = \frac{.017}{.024}$$

giving $n = 2.4$, which appears to be quite reasonable in view of the results obtained by Klemens (1962) and Garber et al (1963).

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